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LOGAN WALLER PAGE, DIRECTOR.

THE DECOMPOSITION OF THE FELDSPARS.

BY

ALLERTON S. CUSHMAN,
ASSISTANT DIRECTOR, OFFICE OF PUBLIC ROADS,
AND
PREVOST HUBBARD,
ASSISTANT CHEMIST, OFFICE OF PUBLIC ROADS.

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THE DECOMPOSITION OF THE FELDSPARS.

INTRODUCTION.

Almost every type of rock which occurs in nature has been used in macadam road building. The results obtained have not always been the same, even when the methods of construction and traffic conditions have been essentially similar. The binding power of rock dust appears to have a relation to the decomposition which the particles undergo when water acts upon them. The feldspars are important constituents of many types of rocks, and their decomposition is therefore a subject of great interest. The results of investigations on the reactions which occur when water acts upon rock dusts have been presented in previous publications by one of the authors,[a] and before proceeding with the description of later results it will be necessary to summarize briefly those already obtained.

The inquiry into the cause of the widely varying cementing or binding qualities of macadam road materials led, in the first place, to a comparison with the similar properties exhibited by clays. When some silicates, such as the feldspars, are reduced to fine powders, they are readily acted upon by water. This has been known for a long time and is generally accepted as accounting for the process of kaolinization by which residual clay deposits have been formed from pegmatites and other feldspathic rocks. Altho the labors of the Rogers,[b] Daubree,[c] Magnus,[d] Forchammer,[e] Brongniart,[f] Fournet,[g] Seger,[h] and others have shed light upon this subject, the mechanism of the decomposition reactions is far from clear. That even freshly distilled water begins immediately to react upon finely ground feldspars, as shown by the use of phenol phthalein, indicates that hydrolysis takes place in case of many rock powders the moment they are wet. It has been found in our own work that by wet grinding in mechanical ball or pebble mills the binding power of most rock powders is greatly increased. The microscopic investigation of wet ground powders shows the surface of the crystalline particles covered with cloggy films composed of hydrated colloidal or pectoidal silicates. These observations are in accord with the results obtained by Daubree, who revolved fragments of feldspar in iron cylinders containing water for protracted periods. It was found that there was invariably a certain amount of decomposition and small amounts of potash past into solution. The resulting fine mud or slime became hard on desiccation and could not be broken up again except with the aid of a hammer. When powdered dry and subsequently treated with water Daubree failed to notice solvent action, altho it does take place to a slight extent, as can be easily shown.

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[a] U. S. Dept. Agr., Bureau of Chemistry Bul. No. 92; Office of Public Roads, Circ. No. 38.

[b] Am. Jour. Sci., 1848, 2d ser. **5**, 401.

[c] Geologie Experimentale, p. 268.

[d] Jour. prakt. Chem., 1850, **50**, 65.

[e] Cited by Ebelmen Ann. Mines, 1845, 4 ser. **7**, 49.

[f] Arch. Muséum d'hist. naturelle, Paris, 1839, **1**, 243; Id. 1841, **2**, 217.

[g] Ann. chim. phys., 1833, **55**, 225.

[h] Collected Writings, v. 1, p. 1.

Since the feldspars contain comparatively large quantities of the soluble alkaline and alkaline-earth bases, it was thought that an estimation of the soluble salts would permit the degree of decomposition in both dry and wet ground powders to be determined. Our work has shown, however, that the analysis of the solution can not furnish a measure of the limits of the reactions which take place. The reasons for this will appear later.

It has always been a source of surprise to investigators who have made a special study of clays that these deposits almost invariably carry a certain percentage of the soluble alkalies, especially potash, in spite of the leaching action of water which they have undergone for enormous periods. If the clay bodies contained mineral particles still undecomposed this could be accounted for, but the microscope shows that this is not always the case. Seger,[a] on comparing the results of complete and rational analyses which he had made upon a large number of plastic clays, noted that those which showed a high proportion of potash contained a smaller amount of absorbed or combined water than those in which the alkali content had almost completely vanished. Hence he thought himself justified in concluding that these mutually displace each other. It is now well known that the so-called "combined water" of a clay body is absorbed into the structure of the clay particles.

The amount of water that is present after all adherent or superficial moisture is removed, is conditioned by an equilibrium between the indrawing effect of the active clay structure and the vapor pressure of the surrounding atmosphere. But it has also been shown that many active clay bodies have the power of indrawing or absorbing the basic ions from solutions of electrolytes, and that in respect to some bases, among which is potash, this activity is especially ronounced. In view of this fact it is apparent that the amount of oluble bases retained will be determined by the equilibrium between the absorptive power of the clay body and the tendency of the ions to wander, either on account of their solution pressure or for any other reason. The absorptive action of some clays is also shown by their power to act as lakes in carrying down certain coloring matters from solutions. This property is possest to a much greater degree by rock powders that have been wet ground than by dry ground powders, and is undoubtedly due to the pectoidal decomposition products.

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[a] Collected Writings, v. 1, p. 75.

Merrill[a] has pointed out that Brongniart, Fournet, and others explained more than fifty years ago the process of feldspathic disintegration thru the breaking up of the feldspar molecule into alkaline silicates soluble in water and aluminum silicates, which are insoluble. The hydrolysis of the soluble silicates and the selective absorption of the bases by the insoluble silicates have not, however, to our knowledge, been heretofore considered in connection with this subject. In addition to this, it has never been clear why the reaction of water upon finely ground orthoclase, which begins so promptly, should almost entirely cease in a few moments. Protracted soaking of a rock powder yields no stronger solution than can be obtained by a short digestion, in spite of the great solubility of the alkaline bases. It is this fact that has led to the prevailing belief that, altho the feldspars are admittedly attacked by water, the action is too slight to render the alkaline bases available for any practical purpose whatsoever.

Bischof[b] assumes the interaction of carbonic acid gas in order to account for the fixation of the alkaline bases, together with the accompanying segregation of the various forms of silica which are often found in the kaolins.

The stronger mineral acids and also various organic and humus acids have been supposed to aid in the kaolinizing action. Such assumptions do not appear to be necessary or warranted in the light of late laboratory investigations. As a matter of fact dilute hydrochloric acid extracts very little more potash than does water alone. It is now well known that many glasses are more readily acted on by water than they are by acid solutions. The complex silicates, of which the feldspars are a type, are mainly insoluble, even in strong mineral acids, and the explanation of their natural decomposition as due to the action of carbonic, humus, and other weak acids is not satisfactory.

If hydrated aluminum silicate, which constitutes the active base of all clays, has the power of absorbing and holding soluble bases, it should exhibit this power when first formed on the surface of a decomposing particle of feldspar. The analysis of a solution obtained by extracting or leaching a weighed quantity of powdered feldspar would therefore fail to measure the extent to which decomposition has taken place. The analyses of a great number of water extractions of orthoclase ground to pass a 200-mesh sieve have shown that the alkalies actually passing into solution amount to only a few hundredths of 1 per cent of the original weight of feldspar taken. A 100-gram sample of orthoclase dust, thru which 10 liters of water was percolated, upon evaporation of the filtrate and ignition of the residue at a dull red heat, gave a weight of 0.0811 of a gram for the first liter of distilled water past thru and 0.0686 of a gram for the nine succeeding liters, making a total of 0.1497 of a gram. Upon analysis this residue was shown to contain an amount of potash equal to 0.024 per cent of the weight of rock dust taken.

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[a] Rocks, Rock-weathering, and Soils, p. 237.

[b] Chemical and Physical Geology, v. 1, p. 61.

In experiments of this kind the greater part of the small amount of alkali which passes into solution is invariably found in the first portion of the percolating water, the reaction evidently slowing down until it practically ceases. This fact, which has been discust in previous publications, and which has been confirmed by a large number of check experiments, may be stated as follows:

When powdered feldspar is acted upon by pure water, the surfaces of the crystalline particles suffer decomposition. The action rapidly slows down, owing to the formation of clogging films of insoluble hydrated aluminum silicate, which to a certain extent absorb the alkaline bases.

It would follow as a corollary of this generalization that unless modifying factors enter into the reactions, complete decomposition or kaolinization could not take place in nature. The leaching effect of water, even prolonged thru geological epochs, would not suffice for the formation of the enormous bodies of residual clays in which few if any particles of undecomposed feldspar still remain. It can be shown, however, that such modifying factors do exist and are undoubtedly active in nature.

It is quite certain that the decomposition of the feldspars, as well as other complex silicates which appear as rock-forming minerals, can not be considered as simple cases of solution. It has been clearly shown in previous publications that the absorption phenomena and the subsequent removal of the absorbed products are modified by a number of factors in the equilibrium. The development of the knowledge of these absorptions shows that all generalizations and deductions which have been made in the past, based merely upon the study of the solutions obtained after digesting rock powders and similar substances with water and dilute acids, have been in error.

FACTORS WHICH MODIFY THE DECOMPOSITION OF THE FELDSPARS.

The factors which modify the absorptions and amount of solution which result in the laboratory when finely powdered feldspar is acted upon by water may be subdivided under the following headings:

(1) **Mechanical**: Effect of grinding, or some other form of attrition.

(2) **Chemical**: (*a*) Reactions which are carried on by water alone; (*b*) Reactions in which other substances than water take part.

(3) **Physical**: (*a*) Electrolysis with accompanying endosmosis; (*b*) Electrolysis without accompanying endosmosis.

MECHANICAL EFFECTS.

As has already been stated, wet grinding of most rock powders very greatly increases their binding power. This is in line with practical experience in road building, which has shown that a liberal use of water under the steam roller is a great aid in obtaining a compact and well-bonded surface. Wet grinding permits the action of water to go farther than when the dry ground material is leached or soaked with water subsequent to grinding. This is shown qualitatively by the deeper pink color obtained with the use of phenol phthalein upon the wet ground material. Quantitative experiments have invariably shown a much greater accumulation of decomposition products in the wet ground powders than in those which have been merely digested with water.

The wet grinding has been done principally in a large cast-iron mill furnished with two 10-kilogram chilled steel balls, which, as the mill revolves, grind and abrade the surfaces of the particles, thus continually presenting fresh surfaces to the action of the water. Some of the grinding was also done in porcelain pebble mills, where the material was subjected to the action of 4 kilograms of smooth flint pebbles, ranging in size from about three-fourths of an inch to 1½ inches in diameter. The results obtained from this method of grinding were not, as a rule, as satisfactory as those obtained from grinding in the ball mill. This is probably due to the fact that the abrading action of the heavy balls produces a surface condition of the particles more favorable to the decomposing action of water than is produced by the splitting effect of impact between the flint pebbles.

CHEMICAL EFFECTS.

REACTIONS WHICH ARE CARRIED ON BY WATER ALONE.

Altho the binding power, as has been already stated, is much increased by wet grinding and the decomposition is carried further, the amount of alkali which the wet ground material yields to water is not so large as might be expected. This is due to the absorption of the alkalies by the insoluble hydrated silicates formed, which make it impossible to remove the soluble products completely by any ordinary means of filtration. This separation, however, has been accomplished by electrolysis and will be discust later. The percentage composition of the impure orthoclase powder used in most of the experiments, which was fine enough to pass entirely thru a standard 200-mesh sieve and which was available in large quantity in a finely ground and carefully sampled condition, was as follows:

	Per cent.
Silica (SiO_2)	68.29
Alumina (Al_2O_3)	18.27
Potash (K_2O)	9.32
Soda (Na_2O)	3.60
Phosphoric acid (P_2O_5)	0.53
Water (H_2O) 100°+	0.48
Total	100.49

A general idea of the relative proportions of soluble products may be obtained from the first figures in Table I, where it is shown that but 0.025 per cent residue was obtained in the filtrate from a dry ground sample treated with water, while 0.32 per cent residue was obtained from a wet ground sample treated in the same manner.

REACTIONS IN WHICH OTHER SUBSTANCES THAN WATER TAKE PART.

It is well known that the treatment of powered feldspar with more or less dilute solutions of various salts leads to an increased amount of decomposition products passing into solution. The effect of solutions of ammonium salts and a full discussion of the reactions have been given in a previous publication.[a] To recapitulate briefly, it was found that about the same quantity of soluble decomposition products could be extracted from a finely ground feldspar, by treatment with a dilute solution of ammonium chlorid, as could be extracted by electrolysis without subsequent regrinding.

Table I shows the weight of residue obtained by treating 25-gram portions of orthoclase with 100 cc of solutions containing increasing amounts of ammonium chlorid. After digestion for an equal length of time in the cold, the slimes were filtered; aliquot portions of the filtrate were evaporated to dryness and the residues gently ignited to drive off all ammonium salts. Both wet and dry ground samples were used, the wet ground having been carefully dried before weighing.

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[a] U. S. Dept. Agr., Office of Public Roads Circ. No. 38.

TABLE I.—*Orthoclase rock powder treated with solutions of ammonium chlorid.*

Strength of ammonium chlorid solution.	Residues obtained per 100 grams.	
	Dry ground.	Wet ground.
Per cent.	*Gram.*	*Gram.*
0.000	0.025	0.320
0.001	.037	.472
0.010	.074	.500
0.100	.160	.528
1.000	.250	.572
1.500	.266	.580
2.000	.243	.570

In every case the wet ground sample produced a greater amount of residue than the dry ground. The effect of ammonium chlorid does not continue to increase after the solution is made stronger than 1 per cent. The amount of potash passing into solution is not equivalent to the amount of ammonium present, and the reaction which takes place is not simply due to metathesis. In order to see if the reactions would go further at a higher temperature, the extractions were repeated in the following manner: Five-gram portions of both the dry and wet ground samples were treated with 50 cc of ammonium chlorid solutions in flasks of Jena glass fitted with return condensers. The contents of the flasks were boiled vigorously for thirty minutes, and finally filtered and the weight of the residues obtained as before. The results are given in Table II, and show that the higher temperature made little difference in the amount of yield.

TABLE II.—*Orthoclase rock powder treated with solutions of ammonium chlorid and boiled thirty minutes.*

Strength of ammonium chlorid solution.	Weight of residue.		Residue per 100 grams.	
	Dry ground.	Wet ground.	Dry ground.	Wet ground.
Per cent.	*Gram.*	*Gram.*	*Gram.*	*Gram.*
0.5	0.019	0.020	0.380	0.400
2.5	.024	.027	.480	.530

In view of the fact that the ordinary analytical method of determining so-called available alkali in rock powders and similar substances is by extraction with dilute acid and filtration, it seemed desirable to determine to just what extent the action of a strong acid like hydrochloric acid would affect the decomposition of the dry and wet ground samples.

TABLE III.—*Orthoclase rock powder treated with hydrochloric acid.*

Treatment.	Residue per 100 grams.	
	Dry ground.	Wet ground, with ammonium chlorid solution.
	Gram.	*Gram.*
Water, cold	0.03	0.57
n/10 HCL, cold	.29	.56
n/10 HCL, boiled	.48	.82
Concentrated HCL, boiled	.67	....

The results in Table III show conclusively that the decomposing action of a strong mineral acid on the feldspar is not nearly so great as might be expected, and in fact exceeds but slightly that of water alone. The combined action of grinding in the presence of a dilute solution of an ammonium salt and subsequent digestion in tenth normal acid has produced a residue equal to 0.82 per cent of the weight of ground feldspar taken. Without the use of acid. ammonium chlorid solution extracted in one case 0.57 per cent. Even concentrated hydrochloric acid without the use of ammonium chlorid extracted only 0.67 per cent, while water alone extracted 0.32 per cent from the wet ground sample, as shown in Table I. These results indicate what has before been claimed—that in order to explain the decomposition of the feldspars in nature it is not necessary to assume the interaction of acids. The effects produced by dilute solutions of acids and salts may be principally to set free the soluble products of hydrolysis absorbed by the pectoidal decomposition products.

It has been noticed in cases in which macadam roads were being constructed of hard material, such as granite or diabase, which are difficult to bond under the roller, that the surface quickly compacted and gave satisfactory results when treated with a top dressing of limestone screenings.[a] This observation suggested the trial of the cementing power of mixtures of these rocks with limestone. The test for cementing value is made in the laboratory of the Office of Public Roads by grinding the rock powder in a mill for a definite time with sufficient water to make a thick paste. Cylindrical briquettes are then molded in a die under a standard pressure, and, after gradual and thoro drying, are broken in a small impact machine. The number of 1-centimeter drops of a 1-kilogram hammer necessary to cause failure of the briquette is called the cementing value. As compared with the results of service, a cementing value of 10 is low, 20 is fair, 40 is good, and all values above 50 are excellent.

A limestone which gave a cementing value of 20 when ground wet in the mill was mixt in about equal proportions with a granite which had a cementing value of 6. This mixture when ground wet gave a cementing value of 82. Such a large increase in the binding power resulting from mixing two rocks of common occurrence is an important fact to bring out, as it has a direct bearing upon a practical problem in road building. In Table IV the results of a number of tests are given, and show conclusively that the addition of limestone to a feldspathic rock invariably increases the binding power.

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[a] L. W. Page, Selection of Materials for Macadam Roads, Yearbook Dept. Agr., 1900, p. 352.

Table IV.—*Results of tests of the cementing value of granite mixt with limestone.*

Granite.	Limestone.	Cementing value.		
		Granite.	Limestone.	Mixture.
Serial No.	*Serial No.*			
1329	1315	10	13	22
1398	1395	6	20	28
1431	1391	3	27	110
1432	1342	9	22	56
1435	1335	7	26	38
1435	1423	7	26	53
1574	1411	6	20	82

Evidence has been advanced in previous publications to show that the binding power of rock dusts is the result of the decomposition, or hydrolysis, brought about by the action of water. As a logical conclusion it follows that if this binding power can be increased by the addition of limestone it is caused by further decomposition of the material, brought about by the interaction of calcium hydroxid, resulting from the hydrolysis of the limestone particles. To test this point a number of granites were ground with a small quantity of limewater. The results confirmed our expectations. In nearly every case the cementing value was increased, as shown in Table V.

Table V.—*Results of tests of the cementing value of granite mixt with limewater.*

Serial No.	Cementing value.		Serial No.	Cementing value.	
	Alone.	With lime-water.		Alone.	With lime-water.
810	12	21	1276	11	31
811	6	16	1329	10	44
817	11	21	1398	6	18
893	12	16	1431	3	19
1008	35	45	1432	9	12
1192	14	27	1435	7	15
1275	16	39	1574	6	11

The effect of dolomites upon the cementing value of granites was next tried, and while an increase was noted in almost every case, it was not as pronounced as in the granite-limestone mixtures. This is at once evident upon comparison of Table VI with Table IV, as some of the same granites were used in both tests.

Table VI.—*Results of tests of the cementing value of granite mixt with dolomite.*

Granite.	Dolomite.	Cementing value.		
		Gran-ite.	Dolo-mite.	Mix-ture.
Serial No.	*Serial No.*			
1276	1283	11	15	32
1329	1315	10	13	31
1398	1395	6	20	22
1431	1659	3	10	30
1432	1655	9	19	21
1435	1680	7	9	33

From the solubility relations of the two minerals, it is safe to suppose that dolomites hydrolyze to a much less extent than do limestones. Their action should therefore be less pronounced and the cementing value should not be increased to the same extent.

In considering the action of limestone and limewater upon granites, it would seem that if the increased binding power were due to increased decomposition it would be shown by the extraction of a greater quantity of soluble alkalies from feldspathic rock powders. The results in the following table bear out this inference. They were obtained by grinding orthoclase sample No. 1300 with pure lime and gypsum, and extracting weighed amounts of the mixture with water. The residues were not weighed, but the excess of lime was removed as in the Lawrence Smith method; the combined alkalies were then converted to chlorids and weighed, after which the potash was carefully determined in the usual way as potassium platinic chlorid. In each case 5 per cent by weight of the lime compound, in the condition of fine powder, was added to the orthoclase dust, and 2 grams of the mixture was extracted with 25 cc of water for ten hours.

Table VII.—*Potash (K_2O) obtained from mixtures of orthoclase dust with lime.*

Condition.	Potash (K_2O).		
	Total.	Correction.	Actual.
	Per cent.	*Per cent.*	*Per cent.*
Dry ground	0.08	0.00	0.08
	0.12	0.00	0.12
Dry ground with calcium sulphate	0.35	0.02	0.33
	0.35	0.02	0.33
Dry ground with calcium oxid	0.63	0.04	0.59
	0.69	0.04	0.65

Blank trials made to see whether small amounts of potash were contained in the lime compounds or given up by the Jena glass used, showed it to be necessary to apply a small correction. The interpretation as well as the application of these results present several problems. It is very clearly shown that the admixture of lime compounds has increased the amount of alkaline bases passing into solution from four to five times.

Observations that have been made in the study of plant growth furnish contributory evidence to this discussion. It has long been known that the addition of lime and gypsum exerts in many cases a beneficial effect on crops, even tho lime is not to any great extent an essential plant food. Storer[a] states that gypsum and lime decompose the double silicates of the earth, setting potash free. Another authority[b] says: "The chemical action of gypsum and other salts of lime in setting potash free from insoluble compounds is undoubtedly the only tenable explanation of the wonderful results following their use." It is apparent from these citations that field observations are in accord with the results of laboratory investigations. The solutions of electrolytes, such as the ammonium salts and lime, which it has been shown set free added quantities of alkali from decomposing feldspar, invariably produce coagulations when added to a slime or suspension of the finest particles of feldspar in water. This is an interesting point which will be reserved for discussion later on.

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[a] Agriculture in Some of Its Relations with Chemistry, ed. 1, v. 1, p. 206-216.

[b] New York State Museum, Report of the State Geologist, 1903, p. 120.

PHYSICAL EFFECTS.

ELECTROLYSIS WITH ACCOMPANYING ENDOSMOSIS.

As a result of the investigations already described the following conclusions seem to be warranted:

(1) Water produces an immediate tho slight decomposing action upon finely ground feldspar.

(2) This reaction, due to hydrolysis, very soon slows up and almost entirely ceases, in spite of the fact that the alkaline bases set free are very soluble in water.

(3) The slowing up of the hydrolysis is due to the clogging effect of insoluble aluminum silicate, which is precipitated on the surface of the particles. In this colloidal aluminum silicate the bases are largely held by absorption instead of passing freely into solution.

(4) Wet grinding permits the action to go further by constantly abrading the particles and thus exposing fresh surfaces to the action of the water.

(5) The action of electrolytes is to set free the basic ions absorbed by the colloid decomposition products. This action is not in the nature of chemical metathesis, but is due to a change in the equilibrium conditions of the system.

In view of these considerations, which will be discust more fully in the conclusion of this paper, it seemed possible that by electrolyzing feldspar or other rock dust slimes in a suitable apparatus, the absorbed bases could be removed and the amount of decomposition measured. It does not seem likely that electrolysis can actually cause decomposition in any other way than by removal of the reaction products from the point of formation on the surface of the particles.

In 1840 Brongniart,[a] having advanced the theory that the kaolinization of the feldspars in nature is in part due to electrolytic effects produced by earth currents, devised a simple and interesting experiment. Fine-ground feldspar was slimed with water and placed in a U tube. In one of the arms a strip of zinc was inserted and in the other a strip of copper. The two metal strips were then connected at the top by means of a wire. At the end of fifteen days it was found that while the liquid in the zinc side was still opaque, that on the copper side had settled and was quite clear. At the same time it was noticed that while the zinc was quite neutral, the copper side was decidedly alkaline. This experiment was continued for two years, and at the end of this time the copper arm was found to contain a strong solution of potassium carbonate. The zinc electrode was heavily coated with closely adherent feldspar, while the copper remained quite clean.

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[a] Arch. Muséum d'hist. naturelle, Paris, 1841, 2, 285.

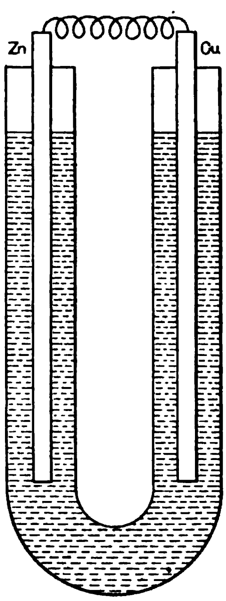

Fig. 1.—Improved form of Brongniart apparatus.

A modified and improved form of the Brongniart apparatus which has been much used by one of the authors for demonstration purposes is shown in figure 1. A little phenol phthalein is mixt with the slime and the whole apparatus is placed in an oven at a temperature of about 100° C. By this means the electrolytic effect becomes clearly apparent in the course of a few hours and can be used as a lecture demonstration. If the slimed feldspar is placed inside an unglazed porcelain cup the electrolytic and endosmotic effect can be very strikingly demonstrated. In figure 2 the slime chamber is made of a thick-walled Pasteur filter tube. Distilled water to which a little phenol phthalein has been added is placed in the outer or cathode compartment.

The anode is a strip of platinum and the cathode is formed of a spiral of fine platinum wire coiled around the porcelain tube. On connecting the apparatus with an ordinary 110-volt direct-current lighting circuit the alkali immediately shows at the spiral cathode, reddening the indicator. At the same time the level of the liquid in the cathode chamber rapidly rises, owing to the endosmotic effect.

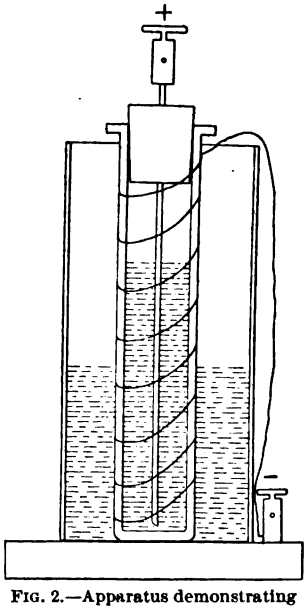

Fig. 2.—Apparatus demonstrating electrolysis and endosmosis of rock powders.

The type of cell used in our earlier quantitative experiments was adopted on account of its simplicity, and answered the purpose very well. The arrangement is shown in cross section in figure 3.

Two hundred grams of the rock powder is slimed with water and placed in the inner or anode chamber, which consists of an unglazed earthenware cup. An arc-light carbon is then inserted and connected to the positive pole of a 110-volt direct-current circuit. The outer compartment, which is of glass or porcelain, contains a quantity of distilled water, into which the carbon cathode is inserted. As soon as the circuit is closed the alkaline ions resulting from the hydrolyzing action of water on the feldspar begin to migrate to the negative pole. The cathode liquor grows rapidly alkaline, as can be readily shown by adding a few drops of a phenol phthalein solution to the water in the outer compartment.

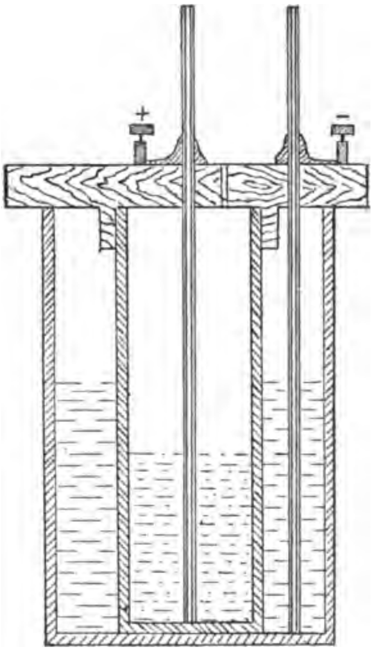

FIG. 3.—Simple form of endosmotic cell.

At first the resistance of the cell is high, the amount of current passing being approximately 0.05 of an ampere on a 110-volt circuit. As the cathode liquor grows stronger the resistance falls, until finally about 0.5 of an ampere passes. As an accompaniment of the electrolysis, endosmosis takes place, the liquid from the slime chamber passes thru the walls of the porous cup into the outer compartment, while the powder itself migrates to the anode. This action finally leaves the powder in a hard dry cake about the anode. At the end of an hour the alkali which has collected in the cathode chamber is titrated with tenth normal nitric acid. The caked material in the anode chamber is then reslimed with water and the electrolysis repeated with fresh water outside.

Successive titrations showed a diminishing yield of alkali, and when this yield reached a very low point electrolysis was discontinued. The sample of rock powder was then reground for a number of hours in a pebble mill, after which a fresh electrolysis was begun. It was found that the yield of alkali started off afresh in the same way as before and gradually diminished until a very low point was reached. Curves for three successive electrolyses made on a 110-volt circuit, which have already appeared in a previous paper,[a] are republished in figure 4, as they furnish an interesting comparison with the curve shown in figure 5, which is a graphical representation of an electrolysis made in the manner described, with the exception that the apparatus was connected with a 220-volt current instead of a 110-volt current, which was ordinarily used in these experiments.

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[a] U. S. Dept. Agr., Office of Public Roads Circ. No. 38.

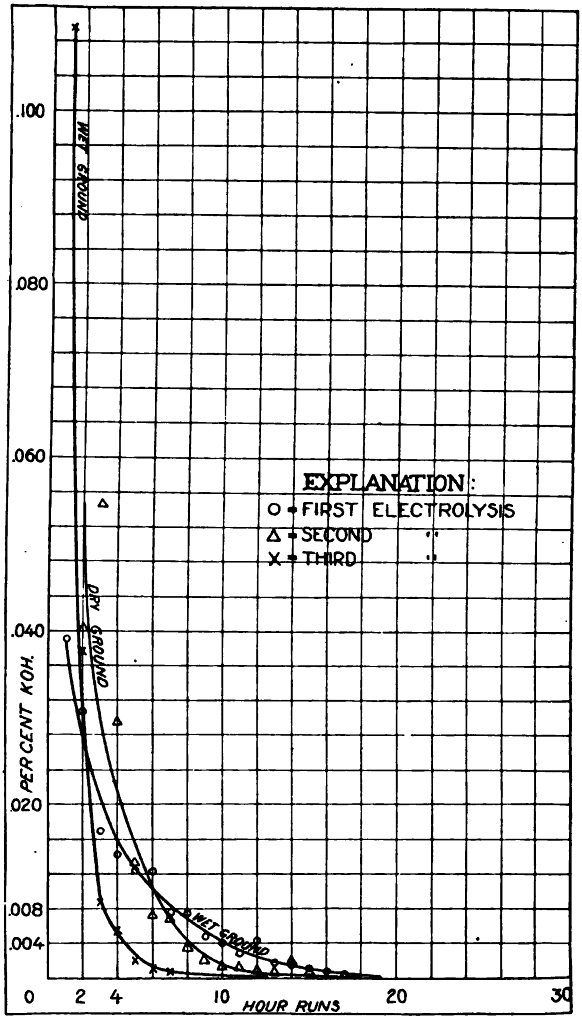

FIG. 4.—Curves showing three electrolyses of orthoclase sample No. 1300.

The only difference noted was that endosmosis took place at a more rapid rate, while the amount of current passing was, of course, doubled. The abscissas represent the separate runs, each run resulting in a complete transfer of the anode liquor to the cathode compartment. The ordinates represent the alkalies extracted, calculated in per cent of potash (K_2O). It will be seen that while the successive yields fall off rapidly for the first few runs, they afterwards do not reach absolutely the zero point, but continue at a very low and almost constant rate. It is also interesting to note that the maximum effect produced, as shown in figure 4, results from regrinding the material wet. There is undoubtedly some maximum degree of fineness which it is possible to attain by regrinding, and up to this point the yields from runs may increase.

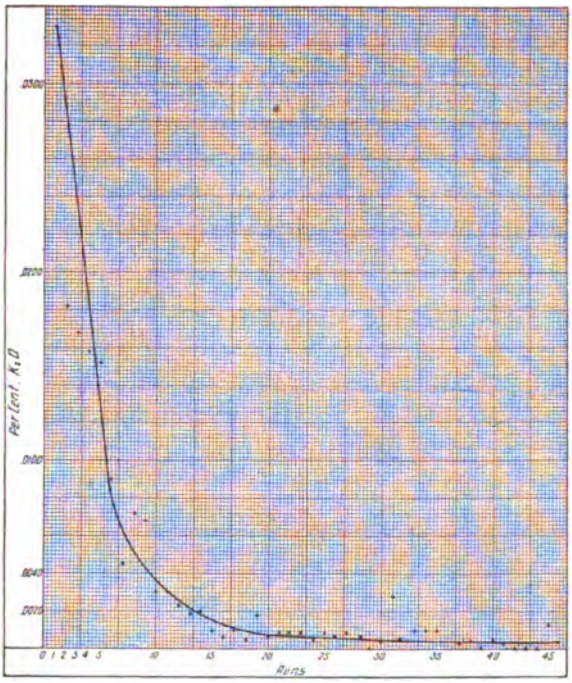

FIG. 5.—Curve showing the electrolysis of orthoclase sample No. 1300 at 220 volts.

Table VIII gives the results of 14 successive grindings and electrolyses of two different feldspars. The total alkalies extracted amount to slightly more than 3.5 per cent of the weight of rock powder taken in each case, and represent complete decomposition of about one-fourth of the material. From these results it seems only fair to presume that the decomposition would undoubtedly be carried to its ultimate conclusion upon further regrinding and electrolysis. Unfortunately the loss due to handling the material was so great that it was found to be impossible to do this work with the sample used.

TABLE VIII.—*Electrolyses of two different feldspars.*

Number of run.	Potash (K_2O) obtained.	
	Sample No. 1242.	Sample No. 1300.
	Per cent.	*Per cent.*
1	0.15	0.14
2	.19	.18
3	.41	.16
4	.13	.14
5	.23	.26
6	.20	.21
7	.16	.17
8	.18	.25
9	0.12	0.15
10	.45	.35
11	.46	.41
12	.43	.27
13	.39	.45
14	.40	.40
Total	3.90	3.54

It was thought that the phenomenon of endosmosis might be used as a measure of rock decomposition, but numerous experiments on measurements of pressure and rate of flow showed that the slightest variation in conditions produced so great an effect upon the results that none worthy of record could be obtained. In carrying out these experiments, however, a type of cell was devised which

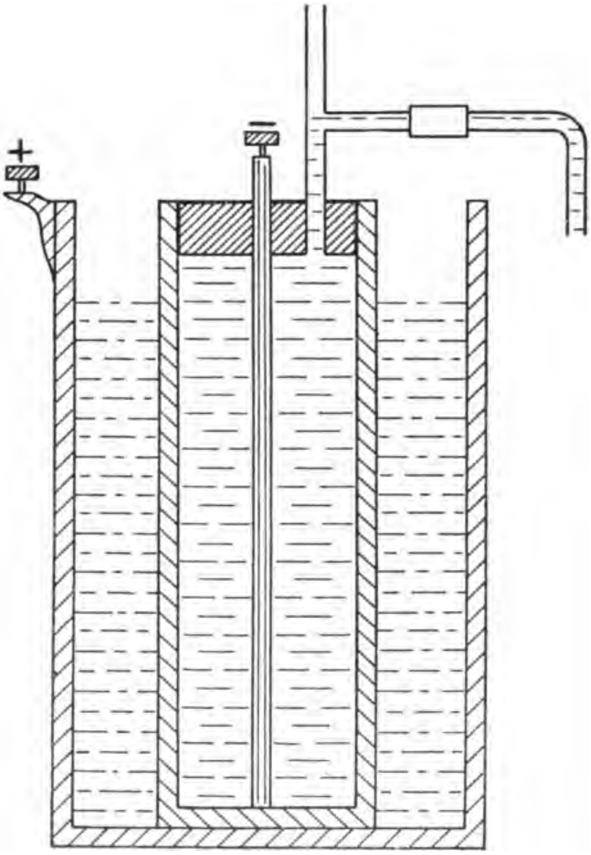

FIG. 6.—Modified form of endosmotic cell.

proved to be so useful in cases where it was desired to remove the products of electrolysis without in any way disturbing the operation that a brief description of it is included here. Figure 6 illustrates this apparatus in cross section. It closely resembles that shown in figure 3, but the operation is here reversed.

The slime to be electrolyzed is placed in the outside compartment, which is made from a tinned can and which serves as the anode. The can used in our experiment was of about 1 gallon capacity. The inner compartment, which consists of a porous cup, is first filled with water and then fitted with a water-tight stopper thru which is inserted a carbon electrode and a glass T joint, the middle limb of which is connected to a piece of glass tubing bent at right angles. As endosmosis takes place, the water is forced out of the cell thru the glass tubing and may be caught in a suitable vessel. The upper limb of the T joint keeps the tube from acting as a siphon and at the same time allows all gas bubbles formed during the electrolysis to escape.

It is well known that the amount of electrical endosmosis that will take place in any cell in which the anode and cathode compartments are separated by a porous diaphragm depends upon a number of factors. The most important of these is the nature of the diaphragm and the concentration or specific resistance of the anode and cathode liquors. In the case of the conditions under which we were working with this apparatus, endosmosis took place more or less rapidly. The apparatus was charged with 4 kilos of ground feldspar in the outer compartment, well slimed with water, while the inner compartment was filled with distilled water. On closing the circuit alkaline water dript rapidly from the overflow tube. The first 100 cc was collected in eleven minutes, but the rate of flow rapidly slowed down as the concentration of the cathode liquor increased. It is probable that the clogging of the pores of the porcelain diaphragm by the slimy material contributed to the slowing down of the action.

After the collection of about 1 liter of the effluent, the rate of flow had decreased to less than 100 cc in eight hours. As soon as 100 cc of the alkaline liquid had been collected, it was titrated with tenth normal nitric acid. The successive readings for the first 10 runs are given in the following table.

TABLE IX.—*Results of titrations.*

Number of run.	Amount collected.	Amount n/10 HNO_3 equivalent.
	cc.	cc.
1	100	4.0
2	100	6.0
3	100	1.8
4	100	18.7
5	100	32.2
6	100	31.6
7	100	30.0
8	100	31.5
9	100	32.1
10	100	30.8

The rate of flow finally became so slow that the use of the earthenware cup was abandoned, and search was made for a diaphragm material which would give better results. After a number of trials it was discovered that cups turned out of wood answered our purpose better than anything else tried. In the earlier experiments the cups which were turned from white pine and poplar were thoroly extracted with alcohol to remove as much of the resinous matter as possible. Subsequently it was determined that the preliminary extraction was an unnecessary operation as the extractive matter was soon eliminated by the preliminary runs, owing to the saponifying action of the alkali. On substituting the wooden in place of the earthenware cups in the apparatus, it was found that electrolysis went on rapidly, but that no endosmosis took place. Common white pine was found to work as well as any other wood, and therefore was generally used. The cups were of various sizes, but the most common form was 18 cm high, 7.5 cm in diameter, with walls 0.5 cm thick.

ELECTROLYSIS WITHOUT ACCOMPANYING ENDOSMOSIS.

Extraction of alkali.—Since endosmosis did not take place with the wooden cups, the stopper and delivery tube were removed from the apparatus shown in figure 6. In other respects the arrangement and charge were similar to those used with the clay cups. Four kilograms of the ground orthoclase were slimed with water and placed in the outer compartment, 200 cc of distilled water was then placed in the wooden cup, and the current from a 110-volt lighting circuit was turned on. From time to time 5 cc of the liquid in the cup was removed and titrated with tenth normal nitric acid. It was found that the alkalies gradually accumulated in the cup until a strength amounting to 32 cc tenth normal nitric acid for 5 cc solution, equal to 3.58 grams potassium hydroxid per 100 cc, was reached. Beyond this point the alkalies would not concentrate. All of the liquid in the cup was then removed and replaced by 100 cc of fresh water. Titrations were again made of 5-cc samples, and again it was found that only a certain concentration of alkalies could be obtained, but this time the concentration point was much lower. The liquid was then removed and the operation repeated a number of times. Each time the maximum concentration obtained was lower than the preceding one. It was found that if electrolysis was continued beyond these points endosmosis began to take place.

In this electrolysis not only a record of titrations was kept, but all of the liquor removed from the cathode chamber was saved. This was eventually evaporated to a convenient bulk and neutralized with nitric acid. It was then filtered and the filtrate concentrated by evaporation to a point where some of the salts began to separate out. These were dissolved in a minimum amount of water, and the solution was allowed to percolate thru a filter into 95 per cent alcohol, where the alkaline nitrates were precipitated. The alcohol was then filtered off and the operation repeated a number of times upon the filtrate. Finally, the whole product obtained was dried at 100° C., cooled and weighed, and a potash determination was made upon a small sample in the usual manner, by precipitation with platinic chlorid. The results were as follows:

Weight of orthoclase electrolyzed	grams	4,000
Weight of crude nitrates obtained	grams	18.77
Potassium (K) found in crude nitrates	per cent	26.50
Actual weight of potassium nitrate (KNO_3) obtained	grams	12.86
Potash (K_2O) extracted from orthoclase	per cent	0.15

In the course of this work special attention was given to see whether or not the soda present in the feldspar was liberated faster than the potash. Titration with tenth normal nitric acid showed a yield of total alkaline oxids of 0.20 per cent. This indicates that the ratio of about 3:1 between the potash and soda, which exists in the original rock, is maintained.

It is shown that we have here a perfectly practical tho hardly an economical process for the extraction and removal of the alkalies from decomposing feldspars. From what has been previously shown, if a grinding effect could be produced in the outer or anode chamber by any suitable means, the action could be made continuous, to the complete kaolinization of the feldspar. Whether or not any action analogous to this takes place in nature we have no means of knowing, but it is certainly within the bounds of possibility, as Brongniart[a] first pointed out.

Altho the apparatus used is somewhat crude, it is probable that the method as outlined could be adapted so as to furnish a much better means of determining the available alkalies in mineral products than any that is now in use by agricultural chemists. Soda and potash that have been set free from the feldspar combination, but which are held by absorption, are undoubtedly available in the sense in which agricultural chemists use the term. The methods of ordinary and at present universal usage which depend upon the leaching or digestion of the material with water or dilute acids are in error, as is shown by the foregoing results. It was hoped that conductivity measurements, carried out by the method used by Briggs,[a] would indicate the relative decomposition of rock powders. Satisfactory results could not, however, be obtained, and the effort was abandoned. It was observed that feldspathic rocks that had been ground with limestone gave a higher conductivity than was given by either material separately. This was interesting, as it confirms the results already given bearing upon the effect of lime on the decomposition of feldspar.

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[a] Loc. cit. (see footnote on p. 17).

Among the numerous problems which this investigation has presented, not the least interesting is the practically complete extraction of potash from the feldspars by the method of electrolysis. The use of wooden cups has enabled us to accomplish this in a very simple manner. The question as to whether or not the process has commercial possibilities need not be discust here.

If hydrofluoric acid of a certain strength is allowed to act on finely powdered orthoclase, the material will be entirely dissolved. For complete decomposition 100 grams of orthoclase would require more than 300 cc of the strongest hydrofluoric acid obtainable. The difficulty of controlling such a vigorous reaction, as well as the expense attached to the use of hydrofluoric acid in large quantities, leaves such a method of attack out of question. In our experiments the apparatus used was similar to that shown in figure 3, except that a wooden cup was made the slime chamber. The slime was prepared by mixing 200 grams of ground orthoclase with 200 cc of water and 20 cc of 35 per cent hydrofluoric acid. In electrolyzing, about 0.5 of an ampere past on a 110-volt circuit. It can readily be seen that the amount of hydrofluoric acid employed was very much less than that needed for total decomposition of the material.

It was found, however, that very nearly total decomposition finally took place. All the bases which are set free, including the alumina, pass thru the diaphragm into the cathode liquor. The alumina is held mainly in solution as an alkaline aluminate and does not appear until the alkaline liquor is neutralized by the addition of an acid, whereupon it is immediately precipitated and quickly settles. If the cathode liquor is made acid with nitric acid at the start the action is very interestingly shown. The resistance of the cell is lowered so that from 1 to 2 amperes pass and the electrolysis proceeds rapidly. As the cathode liquor approaches the neutral point the alumina precipitates as a white cloud, which soon disappears again as the reaction of the liquor passes the neutral point and becomes decidedly alkaline. The results of a typical run, in which this method was used, are given below:

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[a] U. S. Dept. Agr., Bureau of Soils, Bul. No. 15.

Weight of orthoclase electrolyzed	grams	200
Hydrofluoric acid (35 per cent) used	cc	20
Crude nitrates obtained	grams	42
Amount of potassium in crude nitrates	per cent	29.40
Actual weight of potassium nitrate (KNO_3) obtained	grams	31.92
Amount of potash (K_2O) extracted from orthoclase	per cent	7.43

Analysis of the residual material left in the slime chamber after evaporation and drying showed it to contain 1.78 per cent of potash (K_2O), but as only 135 grams remained of the 200 grams of orthoclase used at the start, the potash, calculated on the basis of 200, amounted to 1.20 per cent. This added to the amount extracted gives 8.63 per cent potash, making a loss of 0.69 per cent, which was lost probably by absorption in the colloidal alumina separated and filtered off. Summing up the results of the run, it is seen that of the total potash contained in the orthoclase about 87 per cent was extracted, while 13 per cent remained in the slime. It is probable that the yield could have been still further increased, but toward the end of the run the action is necessarily slow unless a fresh charge of slime is added. For our present purpose the yield is quite high enough to demonstrate the action which is taking place. The reactions which take place in the electrolyzer are undoubtedly complex and are at the present time not perfectly clear. It might be expected that hydrofluo-silicic acid would volatilize and leave the system. The slime frequently becomes hot enough to boil vigorously during the progress of the electrolysis, and yet there is evidence to show that very little hydrofluoric or hydrofluo-silicic acid leaves. It would appear that the hydrofluoric acid is constantly being regenerated and used over and over again.

CONCLUSION.

In a discussion of the decomposition of the feldspars it should be remembered that we are seldom if ever dealing with homogeneous minerals. Potash, soda, and lime replace each other in all proportions in the various types and crystal habits in which the feldspars occur. The influence of chemical composition on the rate of decomposition of these complex silicates is not yet known and offers an attractive field for research. Because the action of water on the large majority of minerals when in a massive condition is extremely slight, they are usually classed as insoluble. Matter in a finely divided state. however, presents a somewhat different proposition, doubtless due to the approach of each particle to its molecular state, with a resulting proportional increase of active surface.

Thus many metals which in their ordinary condition are but slowly oxidized, in the form of a very fine dust oxidize with such extreme rapidity that from the heat of chemical reaction each particle becomes incandescent. So in the case of a rock powder subjected to the action of water immediate reaction takes place. The extent of these reactions seems to depend not only upon the degree of fineness of the powder, but also upon the removal of insoluble decomposition products formed upon the surface of each individual particle. Thus wet grinding has invariably resulted in greater decomposition of a rock powder than has been obtained by dry grinding for the same length of time and subsequent treatment with water. This can only be explained by the constant removal of the insoluble products formed, thus continually presenting fresh surfaces to the action of water.

The discussion of fine powders is usually restricted to material that can pass a sieve containing 200 meshes to the linear inch. It is already possible on a commercial scale, by means of blowers and settling chambers, to separate particles that would pass a 1,000-mesh sieve, were such a sieve mechanically possible. There must be some ultimate limit to the fineness to which it is possible to reduce material by mechanical means. How large are these ultimate particles and what influence does extreme fineness have on readiness to decompose under the action of water? These are questions of great importance.

Portland cement is in a condition of stable equilibrium only when perfectly dry. When water is added decomposition begins at once, leading to an entirely new arrangement. The same is true of many minerals of the type we are studying, except that, for the reasons outlined, the reactions do not proceed to a definite end point in a short period of time. In fact, the analogy goes further, as it is now probable that the pectoidal decomposition products of Portland cement play as important a rôle in the setting as does the crystallizing calcic hydroxid.[a] The influence of fineness on the rate of decomposition of cement is well known, and it is hoped that data will soon be available covering the same subject in regard to rock powders.

It is apparent that in the decomposition of feldspar under the action of water we are dealing not with an equilibrium in a simple two-phase system, such as would be represented by a solvent and a solute. The absorptive power of the pectoid decomposition products, such as aluminum silicate, is acting against the solution tension of the soluble bases. Unless modifying factors appear, the reactions almost entirely cease, even if fresh water is continually presented to the surface of the particles. It has been shown that wet grinding and electrolysis tend to carry on the reactions in the first case by abrasion and in the other by overcoming the absorptive power of the pectoids. When substances other than water react with rock powders, explanation of the observed results becomes more difficult.

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[a] Baumaterialienkunde 1906, **11,** 15.

For a long time it has been known that certain substances, such as alum, ammonium chlorid, limewater, etc., cause a sedimentation of suspended particles of clay and other mineral bodies. This action is readily illustrated by shaking finely-ground rock powder with distilled water in a tall glass cylinder. After the main body of the material has settled, it will be found that the supernatant liquid remains permanently cloudy. Upon the addition of a small quantity of limewater, however, immediate sedimentation takes place and the liquid soon becomes clear. This action may possibly be due to the coagulating effect of the electrolyte, accompanied by shrinkage of the pectoids adhering to the suspended particles. If this shrinkage takes place, fresh surfaces of the underlying particle would be exposed to the action of the surrounding water, which would result in the formation of an increased amount of both soluble and insoluble decomposition products, and these reactions would be repeated until the accumulated decomposition products brought them to a standstill.

The figures given in the foregoing tables prove that these results are actually brought about, as shown by the gain in cementing value and increase in yield of alkalies when a rock powder is ground with limewater or a lime compound. In addition it is possible that the tendency of lime and silica to form insoluble compounds may tend to carry the reaction further. The presence of an excess of ions, however, not common to those set free as a result of the hydrolysis, would account for the passing into solution of an additional amount of the alkaline bases of the feldspar.

The results of investigations described in this paper may be summarized as follows:

(1) Water acts immediately upon finely powdered feldspars, as can be shown by an indicator, such as phenol phthalein. The reaction does not proceed far, owing to the clogging effect of the unremoved decomposition products.

(2) The soluble alkaline bases set free by the decomposition are prevented from passing into solution by absorption.

(3) The decomposition reactions can be made to go further by mechanical abrasion in the presence of water, by treatment with dilute solutions of certain electrolytes and by electrolysis.

(4) The decomposition of ground feldspar can be made practically complete in the laboratory by properly combining these modifying factors.

(5) The mechanism of the decomposition reactions has also been discust, and views already presented in previous publications are confirmed.

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